2-9145-5

RADIOCHEMICAL DETERMINATIONS FOR TAILINGS REFERENCE MATERIALS

FINAL REPORT

BY

PHYSICS DEPARTMENT

THE UNIVERSITY OF CALGARY

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Extraction Procedure

For the determination of all radionuclides with the exception of ^{228}Ra, the samples UTS-1, 2, 3, 4 and 5 were brought into solution by fusion with KF followed by pyrosulphate fusion. This procedure has been described in the report submitted at the conclusion of the previous contract, "Determination of Radium-226 in Uranium Bearing Reference Materials for Certification Purposes", in January 1983 (DSS Contract No. OSQ82-0085).

In addition to the ^{133}Ba tracer, for monitoring the recovery of $Ra/BaSO_4$ in the ^{226}Ra determination: ^{208}Po and ^{228}Th tracers were used for the determinations of $^{210}Pb/^{208}Po$ and $^{230}Th/^{228}Th$ activity ratios.

Since the procedures for the determination of ^{226}Ra (Tables 2-7) were precisely the same as in the previous contract, the details will not be presented here. In what follows, we describe the procedures adopted for the determination of the other radionuclides required in this present project.

Thorium Isotopes

It was decided that the reference standard for thorium would be obtained from a known weight of thorium nitrate. From the weight of this substance and the disintegration constant of ^{232}Th = $1.56 \times 10^{-18} sec^{-1}$, we derived the absolute activity as ^{232}Th of an aliquot of solution prepared from this thorum nirate. Since the exact date of manufacture of the thorium nitrate was not available (only that it was pre-1967), we determined the ratio of ^{228}Th to ^{232}Th in this substance, by measuring this ratio as a function of

increasing additions of ^{228}Th tracer to the standard solution. The activity of the ^{228}Th tracer and the ratio of activities $^{228}Th/^{232}Th$ in the solution prepared from ThO_2 can then be derived from the slope and intercept of the regression line.

If r = ratio of $^{228}Th/^{232}Th$ in the standard solution

t = activity per ml. of ^{228}Th in the tracer solution

p = calculated activity of ^{232}Th in the standard solution

and y = ratio of $^{228}Th/^{232}Th$ activities measured after the addition of x ml. of ^{228}Th tracer,

then we have the following equation:

$$y = \frac{tx + rp}{p}$$

whence if y is plotted against x (data see Table 1), the resultant line should have

$$\text{slope} = \frac{t}{p} = \frac{\text{Activity of } ^{228}\text{Th in tracer/ml.}}{\text{Activity of } ^{232}\text{Th in Standard}}$$

intercept = r = ratio of $^{228}Th/^{232}Th$ activity in standard.

Thus we standardized the ^{228}Th tracer solution and determined the parameter r to be 0.885 ±.005 (in good agreement with the estimated age of the chemical assuming no ^{228}Ra originally).

For the measurement of ^{230}Th, we used ^{228}Th tracer. This has the drawback that if ^{228}Th is present in the sample, corrections must be made to the ^{230}Th activity that is derived. On the other hand, only the sample UTS-5 contained sufficient activity as ^{228}Th to require significant corrections to be made in this regard.

The procedure for extracting thorium from the samples was as follows. After the reprecipitation of $Ba/RaSO_4$ from the EDTA solution with glacial acetic acid, the remaining liquid was reserved. To this solution, 50 μg of cerous ion was added and the solution taken to pH > 13 by the addition of 10M NaOH. At this high degree of alkalinity, cerous hydroxide is precipitated and carries the thorium out of the EDTA complex. The cerium/thorium precipitate was filtered on to 0.1 micron 'Tuffryn' membrane and counted in the alpha particle spectrometer. For the determination of ^{230}Th, (Tables 8-12) ^{228}Th (standardized by means of thorium nitrate) was added to the sample prior to fusion and the activity ratio of $^{230}Th/^{228}Th$ was measured from the peaks in the alpha particle energy spectrum In the case of samples UTS 1, 2 and 5, the activities of ^{232}Th and ^{228}Th were measured relative to the activity of ^{230}Th in samples to which no ^{228}Th tracer had been added.

Polonium/Lead 210

The tracer ^{208}Po is available (Amersham) for the determination of ^{210}Po. Polonium was extracted by adding 50 μg tellurium ion and reducing the solution with sulphur dioxide (by the addition of potassium bisulphite to the acid solution) followed by 15% titanous trichloride. The precipitated metallic tellurium carrying polonium was filtered on to a 0.1 micron membrane and counted in the alpha spectrometer. The ^{208}Po and ^{210}Po peaks were sufficiently well resolved to determine the sample/tracer ratio.

As regards ^{210}Pb, our laboratory is not equipped with

suitable beta counting equipment to determine ^{210}Po via ^{210}Bi. We had anticipated measuring ^{210}Pb using the Ge(Li) spectrometer to determine the 47 keV emission. Unfortunately K-emission lines from heavy elements in the sample interfered with this procedure.

Since ^{210}Po activities were determined in January 1983, (Tables 13-17) we repeated the determinations in March 1983; and thus since ^{210}Po has a 138 day half-life, we were able to derive by calculation the supporting activity of ^{210}Pb, by means of the following calculation:

If $A_{Po}(o)$ and $A_{Po}(t)$ are the polonium 210 activities at the start and end of a storage time t, the lead 210 activity is given by:

$$A_{Pb} = \frac{A_{Po}(t) - e^{-\lambda t} A_{Po}(o)}{(1 - e^{-\lambda t})}$$

In this study $t = 85 \pm 3$ days, λ is the decay constant of ^{210}Po based on a half-life of 138 days, whence:

$$A_{Pb} = 2.88\ A_{Po}(t) - 1.88\ A_{Po}(o)$$

and $$6^2_{Pb} = (2.88)^2\ 6^2_{Po}(t) + (1.88)^2\ 6^2_{Po}(o)$$

Radium 228

This isotope decays into the short-lived actinium 228 (half-life 6.1 hours). Normally ^{228}Ra is determined from the beta activity of ^{228}Ac. We have preferred to use gamma ray spectrometry on 50 gram samples by measuring the strength of the ^{228}Ac line at 0.908 MeV. All samples were pressed into 5 cm.-

diameter, 2 cm.-thick discs with a 20,000 lb. press in order to avoid density corrections. Counting times of 18 hours were required to achieve acceptable counting statistics.

TABLE 1

Standardization of ^{228}Th Tracer Solution

^{228}Th Tracer * Added ml. (x)	Counts in ^{232}Th Peak	Counts in ^{228}Th Peak	Ratio $^{228}Th/^{232}Th$ Activities (y)
0	12621	11067	0.88 ± 0.01
0.5	2728	3164	1.16 ± 0.03
1.0	1584	2194	1.39 ± 0.05
1.5	11310	17758	1.57 ± 0.02
2.0	1599	2763	1.73 ± 0.05
2.5	1450	2797	1.93 ± 0.06

Weighted $\left(\frac{1}{\sigma_i^2}\right)$ least squares fit line.

$y = 0.446\ x + 0.885$ $\rho = 0.995$

The thorium standard solution contained

210 μg of Th = 5.45×10^{17} nuclei of ^{232}Th

= 0.85 Bq ($\lambda = 1.56 \times 10^{-18} sec^{-1}$)

* The ^{228}Th tracer solution was diluted 1:100 and thus the full strength solution contains:

$0.446 \times 0.85 \times 100 = 37.9$ Bq ml^{-1}

± 0.3

TABLE 2

UTS-1

Radium 226

Sample	Mass g	Counting Time Secs.	Radium Counts	% Recovery Ba133	Rate/g
1	1.0136	17000	14347	85.43 ± 0.47	58.48 ± 0.49
2	1.0284	12000	10126	90.63 ± 0.49	54.32 ± 0.54
3	1.0107	58000	47867	85.59 ± 0.47	57.24 ± 0.27
4	1.0082	60000	55073	87.73 ± 0.47	62.26 ± 0.27

Weighted mean $\left(\frac{1}{6^2}\right)$ = 59.07 ± 1.69 counts g^{-1} min^{-1}

Derived ^{226}Ra Content = 3.91 ± 0.09 Bq/g

TABLE 3

UTS-2

Radium 226

Sample	Mass g	Counting Time Secs.	Radium Counts	% Recovery Ba133	Rate/g
1	1.0021	61500	82513	83.60 ± 0.46	94.21 ± 0.34
2	1.0086	11000	13984	85.89 ± 0.47	88.05 ± 0.75
3	1.0187	58000	79425	88.21 ± 0.47	91.44 ± 0.34
4	1.0099	10000	13812	89.71 ± 0.48	91.47 ± 0.78

Weighted mean $\left(\frac{1}{\delta^2}\right)$ = 92.31 ± 1.22 counts g^{-1} min^{-1}

Derived ^{226}Ra content = 6.12 ± 0.08Bq/g

TABLE 4

UTS-3

Radium 226

Sample	Mass g	Counting Time Secs.	Radium Counts	% Recovery Ba133	Rate/g
1	1.0065	18000	57341	87.60 ± 0.47	216.78 ± 0.93
2	1.0280	5800	17166	76.93 ± 0.43	224.55 ± 1.73
3	1.0127	5000	16062	86.95 ± 0.47	218.89 ± 1.74
4	1.0136	7000	17610	71.89 ± 0.41	207.15 ± 1.57

Weighted mean $\left(\frac{1}{6^2}\right)$ = 216.5 ± 3.0 counts g^{-1} min^{-1}

Derived ^{226}Ra content = 14.36 ± 0.15 Bq/g

TABLE 5

UTS-4

Radium 226

Sample	Mass g	Counting Time Secs.	Radium Counts	% Recovery Ba133	Rate/g
1	1.0052	3000	25643	85.76 ± 0.47	594.9 ± 3.8
2	1.0186	3000	19531	63.82 ± 0.38	600.9 ± 4.3
3	1.0252	3600	31761	84.70 ± 0.46	609.6 ± 3.5
4	1.0123	3600	27471	76.75 ± 0.43	589.3 ± 3.6

Weighted Mean $\left(\frac{1}{6^2}\right)$ = 598.8 ± 4.6 counts g^{-1} min^{-1}

Derived ^{226}Ra content = 39.7 ± 0.3 Bq/g

TABLE 6

UTS-5

Radium 226

Sample	Mass g	Counting Time Secs.	Radium Counts	% Recovery Ba133	Rate/g
1	1.0027	58000	200270	82.06 ± 0.45	251.79 ± 0.62
2	1.0102	17700	63475	83.45 ± 0.46	255.24 ± 1.04
3	1.0075	7100	25548	86.01 ± 0.47	249.15 ± 1.58
4	1.0084	5400	19006	83.61 ± 0.46	249.87 ± 1.83

Weighted Mean $\frac{1}{6^2}$ = 252.2 ± 1.1 counts g^{-1} min^{-1}

Derived ^{226}Ra content = 16.73 ± 0.13 Bq/g

TABLE 7

Radium Standard Solution

1 ml of Standard Via Certified Pipette

Sample	Counting Time Secs.	Radium Counts	% Recovery Ba 133	Rate
1	3000	23696	86.65 ± 0.47	546.9 ± 3.6
2	3600	30180	91.62 ± 0.49	549.0 ± 3.2
3	7200	58804	92.47 ± 0.49	530.0 ± 2.3
4	3600	31205	93.14 ± 0.49	588.4 ± 3.3

Weighted Mean $\left(\frac{1}{6^2}\right)$ = 543 ± 13

Radium Standard contains 36.021 Bq/ml (derived from NBS certificate)

TABLE 8

UTS-1

Thorium 230

Sample	Cts. ^{230}Th Peak	Cts. ^{228}Th Peak	Ratio
1	7213	55683	0.129 ± .002
2	2293	19058	0.120 ± .003
3	1934	19808	0.098 ± .002
4	2301	19927	0.115 ± .003

Weighted Mean 0.115 ± 0.015

Derived Th^{230} Content 4.36 ± 0.57 Bq/g

TABLE 9

UTS-2

Thorium 230

Sample	Cts. ^{230}Th Peak	Cts. ^{228}Th Peak	Ratio
1	13831	105624	0.131 ± .001
2	5224	43879	0.119 ± .002
3	4446	35058	0.127 ± .002
4	14852	121639	0.122 ± .001

Weighted Mean 0.126 ± .005

Derived ^{220}Th Content 4.77 ± 0.19 Bq/g

TABLE 10

UTS-3

Thorium 230

Sample	Cts. ^{230}Th Peak	Cts. ^{228}Th Peak	Ratio
1	9170	29984	0.306 ± .004
2	26315	76821	0.343 ± .003
3	8654	23992	0.361 ± .005
4	25807	73689	0.350 ± .003

Weighted Mean 0.340 ± .020

Derived ^{230}Th Content 12.89 ± 0.76 Bq/g

TABLE 11

UTS-4

Thorium 230

Sample	Cts. ^{230}Th Peak	Cts. ^{228}Th Peak	Ratio
1	20277	31698	0.640 ± .006
2	6520	10198	0.639 ± .010
3	10600	16394	0.647 ± .008
4	12997	21266	0.611 ± .007

Weighted Mean 0.633 ± .016

Derived ^{230}Th Content 23.99 ± 0.61 Bq/g

TABLE 12

UTS-5

Thorium 230

Sample	Cts. ^{230}Th Peak	Cts. ^{228}Th Peak	Ratio
1	15889	38485	0.413 ± .004
2	19393	47949	0.405 ± .003
3	9127	21562	0.423 ± .005
4	6295	14611	0.431 ± .007

Weighted Mean 0.413 ± .010

Derived ^{230}Th content 15.54 ± .38 Bq/g

TABLE 13

UTS-1

Polonium 210

Sample	^{210}Po Peak Counts	^{208}Po Peak Counts	Ratio
1	11230	42025	0.267 ± .003
2	2748	9811	0.280 ± .006
3	2748	10707	0.257 ± .005
4	9248	37306	0.248 ± .003

Weighted Mean = 0.260 ± .012

Derived ^{210}Po Content 3.50 ± 0.16 Bq/g (January 2, 1983)

Standard ^{208}Po solution activity derived from Amersham value (quoted to ± 5%) and corrected for radioactive decay.

TABLE 14

UTS-2

Polonium 210

Sample	^{210}Po Peak Counts	^{208}Po Peak Counts	Ratio
1	2410	5962	0.404 ± .010
2	3440	8528	0.403 ± .008
3	3002	7101	0.423 ± .009
4	3895	9504	0.410 ± .008

Weighted Mean = 0.410 ± .009

Derived ^{210}Po Content 5.52 ± 0.12 Cq/g (January 2, 1983)

TABLE 15

UTS-3

Polonium 210

Sample	^{210}Po Peak Counts	^{208}Po Peak Counts	Ratio
1	18722	21410	0.874 ± .008
2	4873	5942	0.820 ± .015
3	5837	7020	0.831 ± .014
4	4893	5871	0.833 ± .016

Weighted mean = 0.853 ± .027

Derived ^{210}Po Content 11.49 ± 0.36 Bq/g (January 3, 1983)

TABLE 16

UTS-4

Polonium 210

Sample	^{210}Po Peak Counts	^{208}Po Peak Counts	Ratio
1	21079	8052	2.61 ± .03
2	7444	2657	2.80 ± .06
3	6918	2910	2.38 ± .05
4	7725	2785	2.77 ± .06

Weighted Mean = 1.61 ± 0.16

Derived ^{210}Po content 35.2 ± 2.1 Bq/g (January 4, 1983)

TABLE 17

UTS-5

Polonium 210

Sample	^{210}Po Peak Counts	^{208}Po Peak Counts	Ratio
1	21838	20741	1.05 ± .01
2	5192	4738	1.09 ± .02
3	5918	5232	1.13 ± .02
4	5054	4690	1.08 ± .02

Weighted Mean = 1.07 ± .03

Derived ^{210}Po content 14.4 ± 0.4 Bq/g (January 4, 1983).

TABLE 18

Determination of ^{228}Ra by Gamma Ray Spectrometry of the Prompt Daughter ^{228}Ac (6.1 hr.)

Thorium Standard

Thorium oxide mixed with silica containing 0.211 g ThO_2 equivalent to 749 Bq.

Sample	Wt. g	Counting Time Hrs.	Net Counts ^{228}AC line at 911 keV	Ratio
Standard	21.09	18	107833	-
UTS-1	74.31	18	8553	0.0733 ± .0007
UTS-2	49.96	18	10178	0.0843 ± .0007
UTS-5	44.13	18	19393	0.174 ± .001
Background	-	18	705	-

Derived ^{228}Ac (^{228}Ra) Activities

UTS-1 0.736 ± 0.007 Bq/g

UTS-2 1.26 ± 0.01 Bq/g

UTS-5 2.95 ± 0.02 Bq/g

TABLE 19

Measurement of Thorium Isotope Activity Ratios

$^{232}Th/^{230}Th$ and $^{228}Th/^{230}Th$

UTS-1

No ^{228}Th Tracer Added

Sample	^{232}Th Counts	^{230}Th Counts	^{228}Th Counts	232/232 Ratio	228/230 Ratio
1	3767	22758	3976	0.165 ± .003	0.174 ± .003
2	5431	31856	5517	0.170 ± .003	0.173 ± .003
3	4879	29312	4952	0.166 ± .003	0.169 ± .003
4	6984	42631	7325	0.164 ± .002	0.171 ± .002
			Wtd. Means	0.166±.003	0.172±.002

Derived Activities (based on ^{230}Th determination of 4.36 ± 0.57 Bq/g)

^{232}Th activity = 0.72 ± 0.08 Bq/g

^{228}Th activity = 0.75 ± 0.08 Bq/g

TABLE 20

Measurement of Thorium Isotope Activity Ratios

$^{232}Th/^{230}Th$ and $^{228}Th/^{230}Th$

UTS-2

No ^{228}Th Tracer Added

Sample	^{232}Th Counts	^{230}Th Counts	^{228}Th Counts	232/232 Ratio	228/230 Ratio
1	3671	16592	3579	0.221 ± .004	0.216 ± .004
2	4657	22319	4713	0.209 ± .003	0.211 ± .003
3	5181	25556	5488	0.203 ± .003	0.215 ± .003
4	4105	19284	4187	0.213 ± .004	0.217 ± .004
			Wtd. Means	0.210±.007	0.214±.003

Derived activities (based on ^{230}Th determination of 4.77 ± 0.19 Bq/g)

^{232}Th activity = 1.00 ± .06 Bq/g

^{228}Th activity = 1.02 ± .05 Bq/g

TABLE 21

Measurement of Thorium Isotope Activity Ratios

$^{232}Th/^{230}Th$ and $^{228}Th/^{230}$

UTS-5

No ^{228}Th Tracer Added

Sample	^{232}Th Counts	^{230}Th Counts	^{228}Th Counts	232/232 Ratio	228/230 Ratio
1	8513	54786	8902	0.155 ± .002	0.163 ± .002
2	5721	37875	5946	0.151 ± .002	0.157 ± .002
3	6386	43654	6701	0.146 ± .002	0.154 ± .002
4	7097	47522	7414	0.149 ± .002	0.156 ± .002
			Wtd. Mean	0.150±.004	0.158±.004

Derived activities (based on ^{230}Th determination of 15.54 ± 0.38 Bq/g)

^{232}Th Activity = 2.33 ± 0.12 Bq/g

^{228}Th Activity = 2.45 ± 0.13 Bq/g

TABLE 22

Redetermination of ^{210}Po after elapsed time of 85 ± 3 days.

Sample	^{210}Po Counts	^{208}Po Counts	Ratio
UTS-1	10002	39174	0.255 ± .003
UTS-2	9769	25417	0.384 ± .005
UTS-3	18320	21546	0.850 ± .009
UTS-4	14632	5871	2.49 ± .04
UTS-5	11113	10545	1.05 ± .01

Derived ^{210}Pb values
(See text for details of calculation)

UTS-1	3.33 ± 0.46 Bq/g
UTS-2	4.51 ± 0.35 Bq/g
UTS-3	11.4 ± 1.1 Bq/g
UTS-4	30.6 ± 4.2 Bq/g
UTS-5	13.8 ± 0.8 Bq/g

Due to contract deadline, we were unable to perform replicates.